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Assistant Commissioner for Patents  
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Pursuant to 37 CFR 1.53(b), transmitted herewith for filing is the patent application of

Inventor(s):

Toshiya KITAMURA

Title:

"NEGATIVE ELECTRODE ACTIVE MATERIAL FOR USE IN ALKALINE CELL AND METHOD OF PREPARING THE SAME"

Priority Claim (35 U.S.C. 119) is made, based upon:

Japanese Patent Application No. 285735/1998 filed October 7, 1998

Enclosed herewith are:

- [X] Specification (Description, Claims, Abstract): Pages 1 - 16; Number of claims 1 - 12
- [X] Declaration and Power of Attorney (executed)
- [X] 2 Sheets of drawings, Figures 1 - 2 [X] Formal [ ] Informal
- [X] Assignment and Form PTO-1595 Recordation Form Cover Sheet and Check for \$40.00
- [ ] Certified copy (ies) of priority document(s) identified above
- [ ] Information Disclosure Statement including Form PTO-1449
- [ ] Preliminary Amendment
- [ ] Verified Statement(s) Claiming Small Entity Status
- [X] Receipt Postcard

	Number Filed		Number Extra	Rate		Calculations
Total Claims	<u>18</u>	- <u>20</u>	=	<u>0</u>	x \$18.00	= \$ <u>-</u>
Independent Claims	<u>6</u>	- <u>3</u>	=	<u>3</u>	x \$78.00	= \$ <u>234.00</u>
MULTIPLE DEPENDENT CLAIMS					+ \$260.00	= \$ <u>260.00</u>
					BASIC FEE	\$ <u>760.00</u>
					Total of above Calculations	\$ <u>1,254.00</u>

To the extent not tendered by check, authorization is given to charge any fees under 37 CFR 1.16 and 1.17 during pendency of the application, or to credit any overpayment, to Deposit Account No. 06-1378. Duplicate copy of this letter is enclosed.

FRISHAUF, HOLTZ, GOODMAN, LANGER & CHICK, P.C.

By:

HERBERT GOODMAN - Reg. No. 17,081

HG/fs  
Encs.

NEGATIVE ELECTRODE ACTIVE MATERIAL FOR USE IN ALKALINE CELL  
AND METHOD OF PREPARING THE SAME  
BACKGROUND OF THE INVENTION

5 The present invention relates to negative electrode active materials for use in  
alkaline cells and, more particularly, to a negative electrode active material for use in  
a cell which is low in gas generation and which is prepared by mixing a metal whose  
valence number of trivalence as its oxide is chemically stable at room temperature  
and atmospheric pressure with an alloyed zinc powder including zinc as a main  
component, and a method of preparing the same. The term "a metal whose valence  
10 number of trivalence as its oxide is chemically stable at room temperature and  
atmospheric pressure" herein used means a metal whose trivalent compound such as  
an oxide thereof is chemically stable at room temperature and atmospheric pressure.

SCANNED 5  
15 Zinc has been favorably used as a negative electrode active material since it  
has an appropriate potential when used as a negative electrode for a cell in an  
aqueous solution system, as well as it is low-priced. However, its corrosion potential  
is more base than the decomposition potential of water so that, when it contacts an  
electrolytic solution, zinc corrosion and decomposition of water occur to generate a  
hydrogen gas. Such hydrogen gas generation not only reduces cell capacity of zinc as  
a negative electrode material, but also, when used in a closed-type cell, increases an  
20 inner pressure of the cell to bring about leakage of the electrolytic solution therefrom  
and, in a worst case, burst of the cell.

Heretofore hydrogen generation has been controlled by alloying zinc, surface  
treatment of zinc particles, adopting a suitable composition of electrolytic solution  
and addition of a corrosion inhibitor to the electrolytic solution. In other words, at  
25 alloying zinc, a zinc alloy including some components selected from the group

consisting of Al, Bi, In, Ga, Sn, Pb and the like has primarily been used in a manner that a composition ratio of these elements is optimized relative to gas generation. However, it is a present situation that such optimization ratio is not enough to solve the problems.

5           Moreover, although a method of adding an indium compound such as indium oxide, indium hydroxide or the like, or a bismuth compound such as bismuth oxide, bismuth hydroxide or the like to an electrolyte gel has been proposed, this method is hardly expected to provide a stable effect and, in addition, it necessitates to mix a zinc powder and an additive in the electrolyte gel at the same time whereupon mixing  
10       work of solid and liquid is troublesome.

#### SUMMARY OF THE INVENTION

As described above, alloying zinc and other methods have been performed so as to control hydrogen gas generation; however, it is hard to say that any of them can obtain a fully stable effect. Accordingly, the object of the present invention is to  
15       provide a negative electrode active material for use in a cell which will reduce hydrogen gas generation from zinc to be brought about when it contacts an electrolytic solution and a method of producing the same.

The present inventor has conducted intensive studies in order to solve the aforementioned problems of the prior art and has found that the addition of a metal  
20       having trivalence to an alloyed zinc powder by the dry mixing method, in more particularly, the addition of a metallic powder of either Bi or In to the conventional alloyed zinc powder for use in a cell by the dry mixing method, preferably in a range of 50 – 1000 (ppm) based on the weight of the alloyed zinc powder, can substantially improve the characteristics of the mixed product which is a powder for use in a  
25       cell showing low hydrogen gas generation; hence, the present invention has been

accomplished on the basis of this finding.

In accordance with one aspect of the present invention, there is provided a negative electrode active material for use in an alkaline cell comprising a composition composed by mixing a metal whose valence number of trivalence is  
5 chemically stable as an oxide thereof at room temperature and atmospheric pressure with a zinc alloy powder for use in a cell.

In accordance with another aspect of the present invention, there is provided a negative electrode active material for use in an alkaline cell comprising a composition composed by mixing a metal whose valence number of trivalence as an  
10 oxide thereof is chemically stable at room temperature and atmospheric pressure with a zinc alloy powder for use in a cell by 50 to 1000 ppm based on the weight of the zinc alloy powder for use in the cell.

In accordance with another aspect of the present invention, there is provided the negative electrode active material for use in the alkaline cell as described above,  
15 in which the metal whose valence number of trivalence as the oxide thereof is chemically stable at the aforementioned room temperature and the aforementioned atmospheric pressure is Bi or In.

In accordance with another aspect of the present invention, there is provided the negative electrode active material for use in the alkaline cell as described above,  
20 in which the metal is a metallic powder with an average particle size of  $100\mu\text{m}$  or less.

In accordance with another aspect of the present invention, there is provided a negative electrode active material for use in an alkaline cell of low gas generation comprising mixing the metallic powder to a zinc alloy powder for use in a cell under  
25 a dry condition.

In accordance with another aspect of the present invention, there is provided a method of preparing a negative electrode active material for use in an alkaline cell comprising a composition composed by mixing a metal whose valence number of trivalence is chemically stable as an oxide thereof at room temperature and atmospheric pressure to a zinc alloy powder for use in a cell.

In accordance with another aspect of the present invention, there is provided a method of preparing a negative electrode active material for use in an alkaline cell comprising the step of mixing a metal whose valence number of trivalence as an oxide thereof is chemically stable at room temperature and atmospheric pressure to a zinc alloy powder for use in a cell by 50 to 1000 ppm based on the weight of the zinc alloy powder for use in the cell.

In accordance with another aspect of the present invention, there is provided the method of preparing the negative electrode active material for use in the alkaline cell as described above, in which the metal whose valence number of trivalence as the oxide thereof is chemically stable at the aforementioned room temperature and under the aforementioned atmospheric pressure is Bi or In.

In accordance with another aspect of the present invention, there is provided the method of preparing the negative electrode active material for use in the alkaline cell as described above, in which the aforementioned metal is a metallic powder with an average particle size of  $100\mu\text{m}$  or less.

In accordance with another aspect of the present invention, there is provided a method of preparing a negative electrode active material for use in an alkaline cell of low gas generation comprising the step of mixing the aforementioned metallic powder to a zinc alloy powder for use in a cell under a dry condition.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph in an embodiment of the present invention showing a relationship between the amount of metallic Bi powder added to the alloyed zinc powder and gas generation amounts; and

Fig. 2 is a graph in an embodiment of the present invention showing a relationship between the amount of metallic In powder and the gas generation amount.

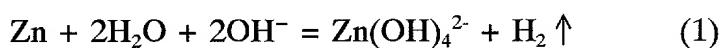
#### DETAILED DESCRIPTION OF THE INVENTION

The trivalent metal-mixed zinc powder according to the present invention can easily be prepared by mixing a trivalent metal powder (with a particle size of under 100  $\mu$ m) such as a powder of Bi, In or the like with a conventional alloyed zinc powder under a dry condition. The product thus obtained is readily available as a zinc powder for use in a cell which is low in hydrogen gas generation.

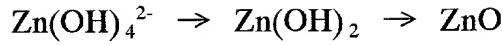
In other words, by mixing of these metallic powders, a negative electrode active material with extremely low hydrogen gas generation which has never been achieved by the alloying method can be obtained. Moreover, by employing the thus prepared trivalent metal-mixed zinc powder as a negative electrode material for use in an alkaline cell, an alkaline cell which is excellent in preservability, storability and safety can be provided.

Mechanism of controlling hydrogen gas generation by mixing the trivalent metallic powders to the zinc powders has not been resolved, but is considered to be as follows:

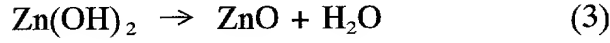
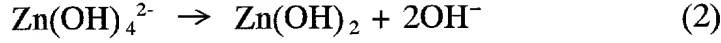
Generally, the reaction of hydrogen gas generation is considered as follows:



$\text{Zn}(\text{OH})_4^{2-}$  ion produced in the above formula (1) undergoes further reaction with an increase in its concentration as follows:



Namely,



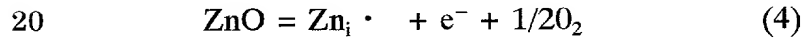
5 The thus produced coating has a construction of Zn/ZnO/Zn(OH)<sub>2</sub>/Zn(OH)<sub>4</sub><sup>2-</sup> in order from the side of electrolytic solution toward the side of zinc.

Since a Zn(OH)<sub>2</sub> coating is of a porous sediment, ZnO basically plays an important role as an anti-corrosive coating. In fact, it is considered that a very thin ZnO coating is formed when zinc contacts the electrolytic solution and, accordingly, a gas generation reaction shown in formula (1) advances by the reaction of Zn which has moved through the ZnO coating to the surface of the electrolytic solution even if zinc is not exposed to the electrolytic solution at a possible crack in the coating.

ZnO is a nonstoichiometric compound of excess Zn type illustrated by Zn<sub>i+δ</sub>O in which excess amount of Zn exists as interstitial ions.

15 The more the amount of interstitial ions, the more the amount of Zn which moves through the ZnO coating to the surface of electrolytic solution and, accordingly, the higher the gas generation shown in formula (1).

An interstitial zinc ion, i.e., Zn<sub>i</sub> · , is formed by a reaction shown in the following formula:



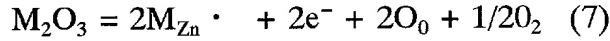
in which equilibrium constant (K) is shown as follows:

$$K = [\text{Zn}_i \cdot] \cdot [\text{e}^-] \cdot \text{P}_{\text{O}_2}^{1/2} \quad (5)$$

It is considered that P<sub>O<sub>2</sub></sub> is constant in this case so that formula (5) can be restated as follows:

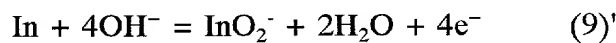
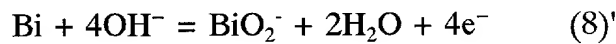
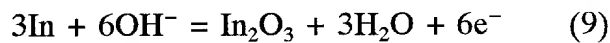
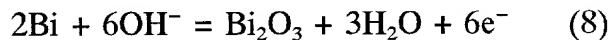
$$25 \quad \text{Ki}' = [\text{Zn}_i \cdot] \cdot [\text{e}^-]$$

If a portion of Zn site of ZnO is substituted with a trivalent ion, i.e.,  $M^{3+}$ , at this point, following formula can be obtained:



Since electrons, i.e.,  $e^-$ , are supplied according to formula (7), the reaction shown in formula (4) advances leftward whereupon the amount of interstitial Zn ions, namely,  $Zn_i \cdot$ , is decreased. Ion species which moves in the coating is this interstitial Zn ion,  $Zn_i \cdot$ , so that the decrease of the amount of  $Zn_i \cdot$  leads to the decrease of the amount of Zn which moves up to the surface of the electrolytic solution thereby resulting in controlling zinc corrosion reaction (which is equal to hydrogen gas generation reaction) shown in formula (1).

Bi and In shown in the present invention become respective trivalent oxides or ions in a high-alkaline electrolytic solution in accordance with the following reactions and then the thus produced ionized chemical species of these dissolve in the ZnO coating to make respective solid solutions through substitutions (reference: M. Pourbaix: "Atlas of Electrochemical Equilibria in Aqueous Solutions" NACE (1974)):



Since electrons,  $e^-$ , are supplied according to formula (7), electrical conductivity of an oxidized coating is increased.

When trivalent ions of metals such as Bi, In and the like are taken into the ZnO coating during the ZnO forming step in which the electrolytic solution and zinc contact each other, hydrogen gas generation will be reduced to increase electrical conductivity of the coating.



In order to produce a Bi or In solid solution effectively in the ZnO forming step, it is necessary for a suitable amount of the powder of one of these metals to be effectively dispersed on the surfaces of zinc particles.

To attain this, it is necessary for an average particle size of the mixed metal  
5 to be  $100\mu\text{m}$  or less and, moreover, its addition is preferably within a range of 50 to 1000 (ppm) based on the weight of zinc alloy powder for use in a cell. If the addition is less than 50 ppm, an effect to be brought about by the addition will not appear. Whereas if the addition is over 1000 ppm, cell capacity will decrease, as well as an effect to be brought about by the addition increment will not appear.

10 Examples and Comparative Examples are provided below for the purpose of further illustrating the present invention, but are in no way to be taken as limiting it and also the alloyed zinc powder composition and the mixed metal powders according to the present invention are by no means limited to being employed in the illustrated Examples and Comparative Examples. Unless otherwise stated, all parts  
15 and percentages are herein given by weight.

#### Comparative Example 1

Alloyed zinc powders with a composition composed of Bi of 89 ppm, Al of 31.1 ppm, In of 516 and the rest of Zn and with particle sizes of 75 to  $850\mu\text{m}$  were prepared by the atomizing method.

20 A 40% KOH electrolytic solution saturated with zinc oxide was added to the thus prepared alloyed zinc powders and kept at  $60^{\circ}\text{C}$ . On the basis of gas generation of the third day, a gas generation amount was calculated (in a unit of  $\mu\text{l/g} \cdot \text{day}$ ). Gas generation measurements have been performed on five pieces of the above-prepared sample. As a result, an average of  $18.32 (\mu\text{l/g} \cdot \text{day})$  and a standard  
25 deviation of  $1.586 (\mu\text{l/g} \cdot \text{day})$  were obtained.

### Example 1

50 ppm, 100 ppm, 300 ppm, 500 ppm and 1000 ppm of the bismuth powder available from Saitama Dowa High-Tech Co. was respectively mixed, based on the weight of the alloyed zinc powder described in Comparative Example 1, with the alloyed zinc powder described in Comparative Example 1 to prepare samples (No. 1 to No. 5) which were then put on the gas generation tests in the same way as in Comparative Example 1. Test results are shown in Table 1. The results are also shown in a graph in Fig. 1.

From the test results, it has been confirmed that mixing of metallic bismuth is effective in controlling gas generation and, particularly, a mixing amount of 500 (ppm) or more is effective for decreasing the gas generation.

Table 1

	(μl/g · day)				
	Addition Amounts of Metallic Bi Powder (ppm)				
	50	100	300	500	1000
No. 1	16.52	16.34	14.61	9.99	10.31
No. 2	14.37	14.80	14.49	7.73	4.67
No. 3	17.53	15.81	14.73	8.21	8.90
No. 4	15.38	15.02	15.90	9.34	11.94
No. 5	14.50	14.3	11.07	6.93	9.77
Average	15.66	15.25	14.16	8.44	9.12
Standard Deviation	1.353	0.815	1.817	1.230	2.722

### Comparative Example 2

Alloyed zinc powder with a composition composed of Bi of 89 ppm, Al of 32.8 ppm, In of 520 and the rest of Zn and with a particle size in the range of 75 to 850 μm was prepared by the atomizing method.

A 40% KOH electrolytic solution saturated with zinc oxide was added to the thus prepared alloyed zinc powder and kept at 60°C. On the basis of gas generation of the third day, a gas generation amount was calculated (in a unit of μl/g · day).

Gas generation measurements have been performed on five pieces of the above-prepared sample in the same way as in Comparative Example 1. As a result, an average of 23.53 ( $\mu\text{l/g} \cdot \text{day}$ ) and a standard deviation of 1.682 ( $\mu\text{l/g} \cdot \text{day}$ ) were obtained.

## 5 Example 2

50 ppm, 100 ppm, 300 ppm, 500 ppm and 1000 ppm each of metallic indium (with purity of 99% or more and particle sizes of less than  $100\mu\text{m}$ ) available from Kojundo Kagaku Kenkyusho was mixed, based on the weight of the alloyed zinc powder described in Comparative Example 2, with the alloyed zinc powders  
10 described in Comparative Example 2 to prepare respective samples (No.1 to No.5) which were then subjected to the gas generation tests in the same way as in Comparative Example 2. Test results are shown in Table 2. The results are also shown in a graph in Fig. 2.

From the test results, it has been confirmed that mixing of metallic indium is  
15 effective in controlling gas generation since the gas generation was gradually decreased with an increase of metallic indium mixing in each sample.

Table 2

	(μl/g · day)				
	Addition Amounts of Metallic In Powder (ppm)				
	50	100	300	500	1000
No. 1	22.67	20.00	22.67	19.33	21.33
No. 2	22.00	22.67	21.33	22.87	18.82
No. 3	22.00	22.72	18.00	20.00	20.33
No. 4	22.00	22.67	23.33	20.09	20.67
No. 5	22.45	20.01	19.45	20.03	19.21
Average	22.22	21.61	20.96	20.46	20.07
Standard Deviation	0.335	1.344	2.372	1.569	1.063

As has been described above, the negative electrode active material for use in  
20 the alkaline cell according to the present invention is easily obtained by mixing a

powder of trivalent metal such as Bi, In or the like with the conventional alloyed zinc powder under a dry condition. The product thus obtained is a zinc powder for use in the cell which shows low hydrogen gas generation, having attained reduction of gas generation to such an extent that it has never been attained by the conventional alloying method and, moreover, the powder is capable of providing an alkaline cell which is excellent in preservability, storability and safety.

5

WHAT IS CLAIMED IS:

1. A negative electrode active material for use in an alkaline cell characterized by comprising a mixture of a zinc alloy powder for use in a cell and an additional metal, wherein said additional metal is a metal whose trivalent compound is chemically stable at room temperature and atmospheric pressure.

2. A negative electrode active material for use in an alkaline cell characterized by comprising a mixture of a zinc alloy powder for use in a cell and an additional metal incorporated therein in an amount of 50 – 1000 ppm by weight based on the amount of said zinc alloy powder for use in a cell, said additional metal being a metal whose trivalent compound is chemically stable at room temperature and atmospheric pressure.

3. The negative electrode active material for use in an alkaline cell according to Claim 1 or 2, wherein said additional metal is Bi or In.

4. The negative electrode active material for use in an alkaline cell according to Claim 1 or 2, wherein said additional metal is a metallic powder with an average particle size of  $100\mu\text{m}$  or less.

5. The negative electrode active material for use in an alkaline cell according to Claim 3, wherein said additional metal is a metallic powder with an average particle size of  $100\mu\text{m}$  or less.

6. A negative electrode active material for use in an alkaline cell of low gas generation comprising a mixture of a metallic powder and a zinc alloy powder for use in a cell, said mixture being prepared by dry mixing said metallic powder and said zinc alloy powder, the metal of said metallic powder being one whose trivalent compound is chemically stable at room temperature and atmospheric pressure.

7. A method of preparing a negative electrode active material for use in an alkaline cell comprising the step of mixing a zinc alloy powder for use in a cell with an additional metal, said additional metal being a metal whose trivalent compound is chemically stable at room temperature and atmospheric pressure.

8. A method of preparing a negative electrode active material for use in an

alkaline cell comprising the step of mixing a zinc alloy powder for use in a cell with an additional metal, said additional metal being a metal whose trivalent compound is chemically stable at room temperature and atmospheric pressure, said additional metal being added in an amount of 50 to 1000 ppm by weight based on the weight of the zinc alloy powder for use in a cell.

9. The method of preparing a negative electrode active material for use in an alkaline cell according to Claim 7 or 8, wherein said additional metal is Bi or In.

10. The method of preparing a negative electrode active material for use in an alkaline cell according to Claim 7 or 8, wherein said additional metal is a metallic powder with an average particle size of  $100\mu\text{m}$  or less.

11. The method of preparing a negative electrode active material for use in an alkaline cell according to Claim 9, wherein said additional metal is a metallic powder with an average particle size of  $100\mu\text{m}$  or less.

12. A method of preparing a negative electrode active material for use in an alkaline cell of low gas generation comprising the step of dry mixing a zinc alloy powder for use in a cell with a powder of an additional metal, said additional metal being a metal whose trivalent compound is chemically stable at room temperature and atmospheric pressure.

12. A method of preparing a negative electrode active material for use in an alkaline cell of low gas generation comprising the step of dry mixing a zinc alloy powder for use in a cell with a powder of an additional metal, said additional metal being a metal whose trivalent compound is chemically stable at room temperature and atmospheric pressure.



## ABSTRACT OF THE DISCLOSURE

A negative electrode active material for use in an alkaline cell which is superior to and lower in hydrogen gas generation than a conventional negative electrode active material obtained by alloying zinc to control the gas generation from zinc to be brought about when it contacts an electrolytic solution and a method of preparing the same. Characteristics of conventional alloyed zinc powders for use in a cell can easily be improved into those of powders suitable for use in the cell which are low in hydrogen gas generation by mixing powders of a trivalent metal, for example, Bi or In, to the conventional alloyed zinc powders for use in the cell, preferably by in a range of 50 to 1000 ppm, under a dry condition.

Fig. 1

Metallic Bi Mixing Effects

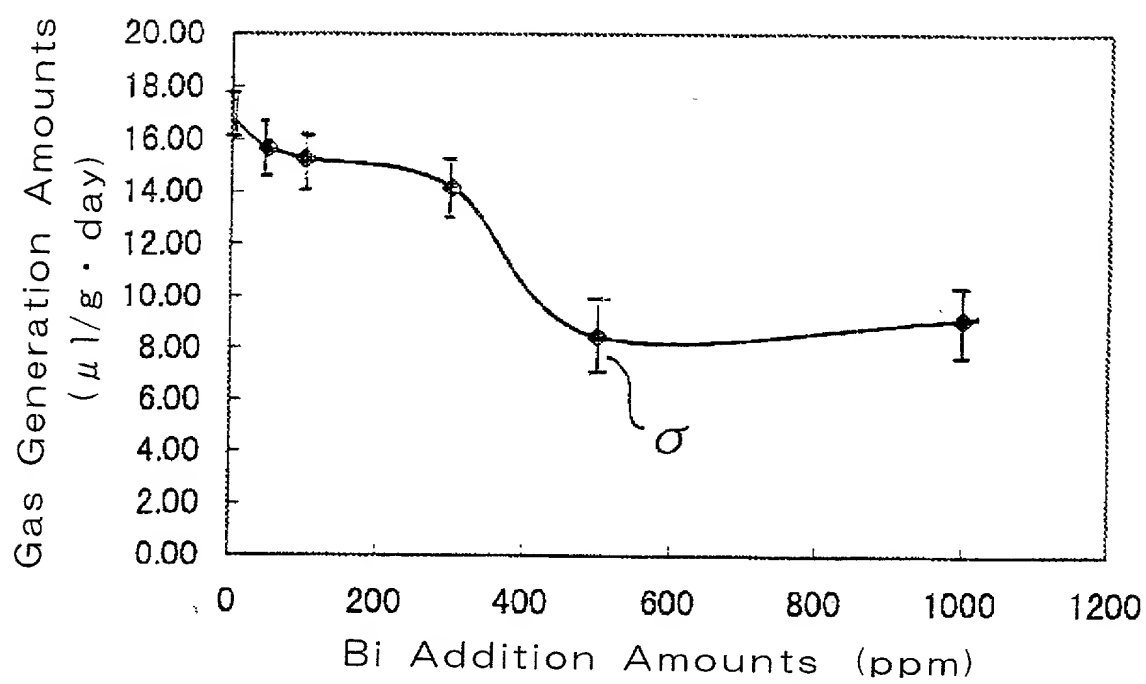
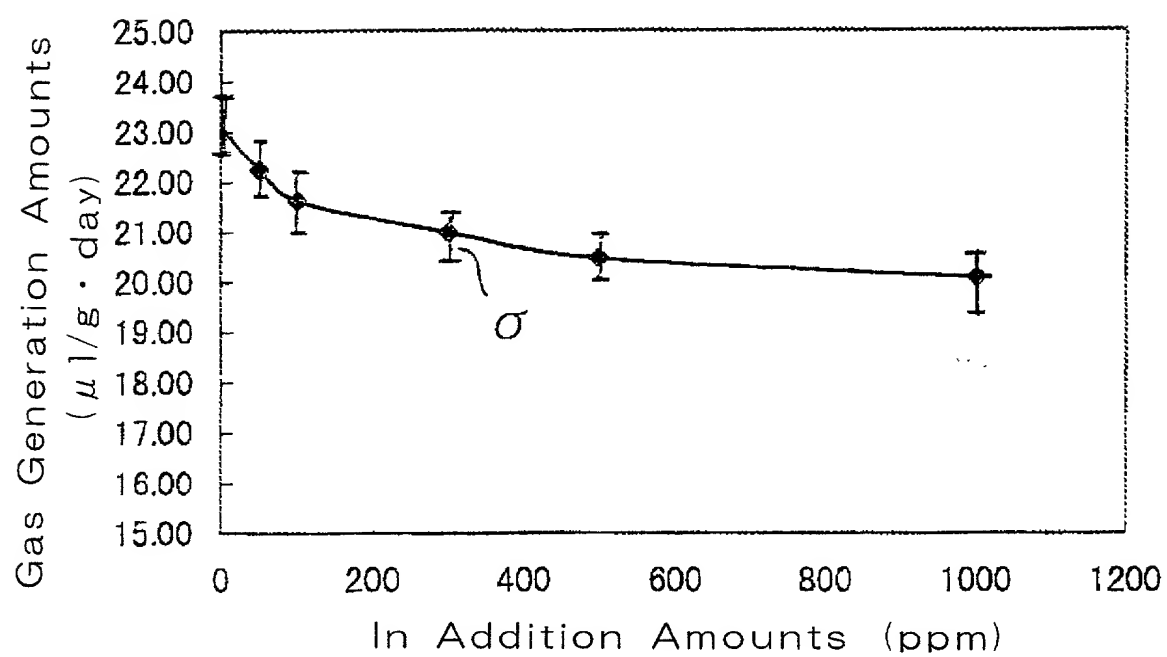


Fig. 2

Metallic In Mixing Effects



**APPLICATION FOR UNITED STATES LETTERS PATENT****Declaration and Power of Attorney**

As a below named inventor, I declare that:

My residence, post office address and citizenship are as stated below next to my name; I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**NEGATIVE ELECTRODE ACTIVE MATERIAL FOR USE IN ALKALINE CELL**

**AND METHOD OF PREPARING THE SAME**

the specification of which is attached hereto.

I have reviewed and understand the contents of said specification, including the claims.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56.

I claim priority benefits under 35 USC §119 of: (i) any foreign application(s) for patent or inventor's certificate listed below; or (ii) any United States provisional application(s) listed below; and have also identified below any foreign application(s) for patent or inventor's certificate, or PCT international application having a filing date before that of the application(s) on which priority is claimed.

COUNTRY	APPLICATION NUMBER	DATE (day, month, year)	PRIORITY CLAIMED
Japan	285735/1998	7/10/1998	yes <u>x</u> no _____
			yes _____ no _____

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I appoint the following attorneys to prosecute this application and to transact all business in the U.S. Patent & Trademark Office connected therewith: Stephen H. Frishauf, Reg. No. 16,233; Leonard Holtz, Reg. No. 22,974; Herbert Goodman, Reg. No. 17,081; Thomas Langer, Reg. No. 27,264; Marshall J. Chick, Reg. No. 26,853; Walter J. Baum, Reg. No. 20,641; Richard S. Barth, Reg. No. 28,180; Douglas Holtz, Reg. No. 33,902; and Robert P. Michal, Reg. No. 35,614.

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**INVENTOR: SIGNATURE****DATE****RESIDENCE AND POST OFFICE ADDRESS**

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Sign:	Date:	Residence (City and Country):
Type:	Citizen of:	Post Office Address:
Sign:	Date:	Residence (City and Country):
Type:	Citizen of:	Post Office Address: